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Coral-Like CoSe₂-Nitrogen-Doped Porous Carbon as Efficient Counter Electrodes for Quantum Dot Sensitized Solar Cells

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Exploration of counter electrode (CE) catalysts with excellent reduction activity to S_n^{2-} and low charge transfer resistance (R_{ct}) is always a major challenge for the development of quantum dot sensitized solar cells. In this work, coral-like $CoSe_2$ - nitrogen-doped porous carbon hydrides ($CoSe_2$ -NC) were successfully prepared by two-step calcination of zeolitic imidazolate framework (ZIF), including carbonization and selenization process. Scanning electron microscopy shows that the $CoSe_2$ -NC catalyst presents a corallike microscopic morphology composed of nanospheres. Electrochemical impedance spectroscopy displays that the $CoSe_2$ -NC CE presents a low R_{ct} of 1.04 Ω . The PCE of the QDSSC based $CoSe_2$ -NC CE is up to 5.06%, which is 26%, 87% higher than those of $CoSe_2$ and NC CEs. The enhanced photovoltaic performance is attributed to the unique coral-like structure and the synergistic catalytic effect of $CoSe_2$ and NC.

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Growing global environmental problems and worsening energy depletion have greatly stimulated worldwide attention to inexpensive renewable energy. Quantum dot sensitized solar cells (QDSSCs) have been considered one of the most promising energy conversion devices, due to the higher theoretical conversion efficiency (44%), ease of fabrication, low-cost raw materials, and other advantages.^{1,2} Typically, a QDSSC is composed of a photoanode, a counter electrode (CE), and an $S_n^{2^2}/S^{2^-}$ redox couples.^{3–5} The photoanode plays the role of harvesting photons to generate and capture electrons. Besides, the CE not only acts as the collector of electrons, but also serves to circulate and reduce $S_n^{2^-}$ in the electrolyte.^{6,7} Recently, a power conversion efficiency (PCE) up to 13.71% has been obtained through quantum dot materials engineering,⁸ however, it is far below its theoretical conversion efficiency. Therefore, there are many challenges in the process of improving the photovoltaic performance of QDSSCs.

As an important component of QDSSCs, counter electrodes have attracted widespread attention from researchers around the world. In common S_n^{2-}/S^{2-} electrolyte systems, conventional platinum catalysts lead to high and irreversibility overpotential during S_n^{2-} reduction due to a strong bonding with S^{2-} ions, which hinders its catalytic performance.⁹ To overcome this obstacle, many alternative catalytic materials have been investigated, such as carbonaceous materials, metal selenides, metal sulfides, spinel sulfides, conducting polymers, etc.^{10–15}

Carbonaceous materials (including carbon nanotubes, graphene, activated carbon, carbon black, etc.) have attracted wider attention, due to their unique physical properties, relative stability, environmental friendliness, and earth abundance.^{12,16–22} However, this catalyst did not achieve the desired reduction activity to S_n^{2-} because the fewer catalytic sites on the sp² carbon framework limited the catalytic activity.²³ To date, several methods are considered to be effective in enhancing the catalytic activity of carbonaceous materials, such as heteroatom doping, morphological control, material compounding, etc.^{24–30} Until now, an update to the highest PCE of QDSSCs has been the use of N-doped mesoporous carbon as the CE, which fully indicates the feasibility and efficiency of carbon materials as CEs for QDSSCs.^{8,31}

Metal-organic frameworks (MOF) have been extensively studied due to the large specific surface area, well-defined morphology, high porosity, and good stability. In common, MOFs are composed of metal ions and organic ligands, and the framework can be adjusted by introducing various organic ligands and metal ions.^{32,33} It has been demonstrated that heteroatom-doped porous carbon obtained by pyrolysis of MOF can be used in electrochemical reduction reactions.⁵ Cui et al. applied CoS₂ embedded carbon nanocages obtained by direct sulfation of ZIF-67 to dye-sensitized solar cells (DSSCs) CE and obtained a PCE of up to 8.20%.³⁴ Wang et al. prepared CoSe₂/NC and CoS₂/NC using ZIF-67 as a self-template. The DSSCs fabricated with CoSe2/NC (CoS2/NC) CEs achieved a PCE of 9.06% (8.74%).³² MOF-derived carbon hybrids combine heteroatom doping and material complexation strategies to further improve the catalytic performance of carbonaceous materials. Until now, numerous studies have shown the outstanding electrocatalytic performance of CoSe₂ - N-doped porous carbons (CoSe₂-NC) in a variety of fields, such as DSSCs, oxygen evolution reaction, and supercapacitors.^{32,33,35} To our knowledge, the reduction properties of CoSe₂-NC CE to S_n^{2-} in QDSSC are little known.

Herein, coral-like CoSe₂-NC hybrids were successfully prepared by the two-step calcination of ZIF, including the carbonization and selenization process (Fig. 1). The prepared CoSe₂-NC hybrid has a large BET surface area (168.4 m²·g⁻¹), which greatly increases the contact with the electrolyte and thus improves the reduction activity to S_n^{2–}. Meanwhile, the QDSSC based on the CdS/CdSe QDs-sensitized photoanode and the CoSe₂-NC CE achieves a PCE of up to 5.06%, which is 26% and 87% higher than that of CoSe₂ and NC CEs, respectively.

Experimental Section

If without special stated, all chemical reagents used in this work were purchased from Aladdin Reagent Co., Ltd. (Sigma-Aldrich) and used without any further purification.

Preparation of Co/Zn-ZIF.—Co/Zn-ZIF was prepared with reference to the previous literature with appropriate modifications.³⁵ In general, 1.164 g of $Co(NO_3)_2 \cdot 6H_2O$ and 1.190 g of $Zn(NO_3)_2 6H_2O$ were dissolved in 50 ml of methanol, and 2.627 g of 2-methylimidazole was also dissolved in 100 ml of methanol, then the solution was stirred at room temperature into a



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Figure 1. Schematic illustration of the preparation of CoSe₂-NC.

homogeneous solution, followed by aging for 24 h. The mixture was separated by suction filtration and washed 3 times with ethanol. Finally, ZIF was dried in a vacuum 60 $^{\circ}$ C for 12 h.

Preparation of CoSe₂-NC.—For the synthesis of CoSe₂-NC precursors (Co-NC), an appropriate amount of Co/Zn ZIF powder was calcined at 800 °C for 3 h in an argon atmosphere. And then after fully grinding and mixing 200 mg of the precursor and 1 g of selenium powder, the mixture was heated to 500 °C for 2 h in a flowing argon atmosphere to prepare CoSe₂-NC material. For comparison, Co-NC precursors were washed with 2 M HCl solution to remove the Zn and Co species, and the obtained black powder is marked as NC.

Preparation of CoSe_2.—The preparation of $CoSe_2$ is the same as that of $CoSe_2$ -NC. The difference was that Co-NC was replaced by cobalt (II) nitrate hexahydrate.

Preparation of CEs.—The as-prepared samples and polyvinylidene fluoride were dispersed in an N-methyl-2-pyrrolidone solvent at a mass ratio of 9:1, and the mixture was fully ground to form a slurry. The obtained slurry was deposited onto cleaned titanium mesh by screen-printing technique to get a 0.25 cm² active area, and then, the coated titanium mesh was dried at 60 °C for 2 h under vacuum.

Preparation of photoanodes and QDSSC devices.—The photoanodes were prepared with reference to our previous work.^{36,37} The prepared photoanodes and CEs were encapsulated with insulating tape to form a sandwich structure, filling with a redox electrolyte composed of 2 M Na₂S, 2 M S, and 0.2 M KCl.

Characterization .- The morphology of the samples was explored with field emission scanning electron microscopy (SEM, Hitachi S4800). The X-ray diffraction (XRD) patterns were obtained using a Purkinjie XD-30 system equipped with Cu k α radiation. The Raman spectra were recorded using a Sierra IM-52 Raman microscope (Snowy Range Instruments) with a laser wavelength of 785 nm. X-ray photoelectron spectroscopy (XPS) measurement was carried out using a Thermo, ESCALAB 250Xi spectrometer using Al K α irradiation as the X-ray source. The specific surface area was tested using the nitrogen adsorption-desorption technique (Micromeritics ASAP 2460). An electrochemical system (Ivium-N-Stat multi-channel) was used to study electrochemical impedance spectroscopy (EIS), Tafel polarization measurement, cyclic voltammetry tests, and photovoltaic performance. The current-voltage characteristic of the QDSSC (J-V curve) was recorded under one sun illumination using HGILX500 technology (AM 1.5 G, 100 mW· cm⁻²) (China) Solar Simulator, calibrated by a commercial organization Standard crystalline silicon solar cells.

Results and Discussion

Structural and morphological characterization.—The micromorphology of CoSe₂-NC was characterized by scanning electron microscopy (SEM). The SEM images of CoSe₂-NC at different magnifications are shown in Figs. 2a–2d. CoSe₂-NC has a porous coral-like morphology formed by the accumulation of nanospheres. This porous coral structure dramatically increases contact with the electrolyte, while network structure formed by interconnected $CoSe_2$ -NC nanospheres also provides a pathway for electron conduction. TEM images (Figs. 2e–2f) show nanospheres with a diameter of about 65 nm. The carbon sheets around the nanospheres may be formed by the carbonization of excess 2-methylimidazole. Energy-dispersive spectroscopy (EDS) elemental mapping images (Fig. 3) display that C, N, Co, and Se elements uniformly disperse on the bulk surface, indicating $CoSe_2$ and N doped porous carbon are uniformly compounded.

N₂ adsorption-desorption isotherms were conducted to analyze the specific surface area and pore size distribution of CoSe₂-NC, NC, and CoSe₂. As shown in Fig. 4a, the CoSe₂-NC sample presents an obvious type-IV isothermal curve along with a typical H3 hysteresis loop, indicating the presence of a mesoporous structure, ^{5,38,39} which can be verified based on the corresponding pore size distribution (Fig. 4b). It can be seen from Fig. 4b that CoSe₂-NC and NC have rich micro-mesoporous structures with an average pore diameter of 3.32 nm and 2.70 nm, which come from a coral-like porous skeleton and MOF-derived unique structure. NC sample has a larger BET surface area of 652.8 $m^2 \cdot g^{-1}$, this is because the cobalt metal particles on the ZIF-derived carbon nanospheres are etched away to create more pore structure. The BET surface area of CoSe₂-NC has decreased compared to NC, but still has a considerable BET surface area (168.4 $m^2 \cdot g^{-1}$), which can provide more catalytically active sites. The BET surface areas of the three samples are listed in Table I.

The XRD patterns were performed to identify the crystallinity and composition of the prepared samples. In Fig. 5a, several main diffraction peaks of CoSe₂-NC and CoSe₂ nanocrystals observed at 30.49° , 34.19° , 37.57° , 43.66° , 51.71° , 56.59° , 58.94° , and 74.09° correspond to the (200), (210), (211), (220), (311), (230), (321) and (421) planes of CoSe₂ (PDF#09-0234), indicating that the CoSe₂ has been successfully synthesized.^{40–42} However, no diffraction peaks of graphitic carbon are observed from the XRD pattern of CoSe₂-NC, which may be due to the low peak intensity of NC. From the XRD pattern of NC, the peaks at 24.23° and 43.45° are attributed to (002) and (101) planes of graphitic carbon, confirming the NC is well graphitized.³³ While, the XRD characteristic peaks of Co, Zn, and its oxides were not observed, which confirmed that Co, Zn species were successfully removed by washing with HCl solution.^{43,44}

Figure 5b shows the Raman spectra of $CoSe_2$ -NC and NC to investigate the defects, interlaminar structure, and doping information of carbon materials. Two broad characteristic peaks can be observed, corresponding to the D and G band, which further demonstrates the presence of graphitic carbon in $CoSe_2$ -NC. Typically, the D band and G band peaks are related to structural defects as well as disorder and sp² bonded carbon atom vibrations, respectively.^{36,45,46} And the ratio of D and G band intensity (I_D/I_G) is usually used to evaluate the defect and graphitization degree of carbon materials.³¹ Compared with the I_D/I_G value of CN (3.37), $CoSe_2$ -NC exhibits a lower value (1.98), demonstrating an increase in graphitization of $CoSe_2$ -NC by double calcination.

The chemical composition and valence states of CoSe₂-NC are investigated by X-ray photoelectron spectroscopy (XPS). The full scan spectrum in Fig. S1 (available online at stacks.iop.org/JSS/10/



Figure 2. (a)-(d) The SEM and (e)-(f) TEM images of CoSe₂-NC.

045012/mmedia) indicates the presence of Co, Se, N, and C in $CoSe_2$ -NC. Figure 6a exhibits the C 1 s high-resolution spectrum, four individual peaks centered at 284.7, 285.6, 286.4, and 289.5 eV are in good agreement with C–C, C–N, C=O, and O=C–O bonds, respectively. Similarly, the N 1 s spectrum in Fig. 6b can be ascribed to three peaks assigned to the pyridinic N (398.8 eV), graphitic N (400.7 eV), and Co–N bond (398.1 eV), severally. The above results show that N atoms have been successfully doped into the carbon skeleton. As shown in Fig. 6c, the two peaks of Co 2p located at

780.2 eV and 796.0 eV are attributed to Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively, proving the presence of divalent cobalt (Co²⁺). Besides, two weak peaks at 778.2 and 792.1 eV with a \approx 15 eV binding energy difference can be observed, those are ascribed to Co $2p_{3/2}$ and Co $2p_{1/2}$ of metallic cobalt.⁴⁷ The Se 3d spectrum (Fig. 6d) can be fitted to three peaks at 54.8 eV and 55.9 eV, corresponding to Se $3d_{5/2}$ and Se $3d_{3/2}$, respectively, which belong to Se₂²⁻ following previously reported results of CoSe₂. Additionally, the peak located at 59.0 eV is related to the Se–O bond at the surface of



Figure 3. SEM image of CoSe₂-NC and its corresponding EDS elemental mapping images of C, N, Co, and Se.



Figure 4. (a) N₂ adsorption/desorption isotherm curves and (b) Pore size distribution curves of all samples.

Samples	BET surface area $(m^2 \cdot g^{-1})$	Pore volume $(cm^3 \cdot g^{-1})$	Average pore diameter (nm)
CoSe ₂ -NC	168.4	0.14	3.32
CoSe ₂	11.6	0.01	3.72
NC	652.8	0.44	2.70

CoSe₂-NC.^{32,33,46} These results indicate that CoSe₂ nanoparticles are successfully anchored on N-doped porous carbon, which further confirms the SEM, XRD, and Raman results.

Electrochemical and photovoltaic characterization.—Typically, cyclic voltammetry (CV) measurements can be used to evaluate the electrocatalytic activity of CE materials, as shown in Fig. 7a, CV tests were carried out with a three-electrode system in an aqueous



Figure 5. (a) XRD patterns of all samples, and (b) Raman spectra of CoSe₂-NC and NC.



Figure 6. (a)-(d) Deconvoluted high-resolution XPS C 1s, N 1s, Co 2p, and Se 3d spectra of CoSe₂-NC.

solution of 0.1 M KCl, 0.1 M Na₂S, and 0.1 M S at a scan rate of 10 mV \cdot s⁻¹. Pt and Ag/AgCl electrodes are counter and reference electrodes, respectively. The anodic peak at the positive side is attributed to the oxidation of S²⁻, and the cathodic peak at the negative side is related to the reduction of S_n²⁻⁵, ⁴⁸ CoSe₂-NC has the highest value of the cathodic current, indicating better electrocatalytic capability toward the polysulfide redox reduction for QDSSCs, which is beneficial for improving the PCE of QDSSCs.

To better confirm the electrocatalytic activity of the CE materials on polysulfide electrolytes, Electrochemical impedance spectroscopy (EIS) and Tafel polarization were performed on a symmetric dummy cell fabricated with two identical CEs. The high-frequency nonzero intercept of the real axis is the series impedance (R_s); the first semicircle represents the charge transfer resistance (R_{ct}) at the interface of counter electrode/electrolyte and the constant phase element (CPE) of the electrical double layer, and the second



Figure 7. (a) CV plots of all samples; (b) Nyquist plots; (c) Bode and (d) Tafel polarization curves for the symmetric dummy cells.

semicircle at the low-frequency region is attributed to the Nernst diffusion impedance (Z_N) in polysulfide electrolyte.⁴⁹ Table II lists the EIS parameters fitted by ZSimpWin software. As shown in Fig. 7b, all samples exhibit low R_s values (3.33–5.09 Ω) due to the excellent contact of the CE materials with the highly conductive titanium mesh. The R_{ct} value of CoSe₂-NC CE is 1.04 Ω , which is significantly lower than CoSe₂ (1.31 Ω) and NC (4.90 Ω). The lowest R_{ct} value of CoSe₂-NC CE indicates the effective reduction of S_n^{2–} to S^{2–}, which may be due to the synergistic effect of the highly catalytically active CoSe₂ and the highly conductive N-doped porous carbon, while the coral-like morphology also increased the contact of CE with the electrolyte. The lifetime (τ_1) of electrons involved in the S_n^{2–} reduction reaction can be obtained by the equation $\tau_1 = 1/2\pi f_p$, where *f* is the peak frequency corresponding to the R_{ct} in the Bode spectrum (Fig. 7c).^{37,50} CoSe₂-NC CE has the shortest τ_1 , demonstrating its excellent S_n^{2–} reduction capability.

Tafel polarization curves are shown in Fig. 7d, CoSe₂-NC CEs show the highest J_0 , indicating a higher exchange current density on the CE surface. And the J_0 values of all samples follow the order of CoSe₂-NC > CoSe₂ > NC. Besides, $J_0 = RT/nFR_{ct}$, indicating J_0 is

Table II. Parameters extracted from EIS of $CoSe_2$ -NC, $CoSe_2$, and NC CEs.

Samples	$\frac{R_{\rm s}}{(\Omega)}$	$R_{\rm ct}$ (Ω)
CoSe ₂ -NC	3.33	1.04
CoSe ₂	3.52	1.31
NC	5.09	4.90

inversely proportional to R_{ct} .³¹ So, the result is consistent with the variation trend of R_{ct} obtained from the EIS and further verify the EIS results.

The photovoltaic performance of QDSSCs based on CoSe2-NC, CoSe2, and NC CEs and CdS/CdSe photoanodes were measured under one simulated sunlight (AM 1.5 G, $100 \text{ mW} \cdot \text{cm}^{-2}$). The short-circuit current density (J_{sc}) , open-circuit voltage (V_{oc}) , fill factor (FF), and power conversion efficiency (PCE) were obtained from the curves, as shown in Fig. 8a and Table III. The QDSSCs based NC and CoSe₂ exhibited low PCE of 2.70% and 4.02%, while the PCE of QDSSCs based on CoSe2-NC is the highest (5.06%), and $J_{\rm sc}$, $V_{\rm oc}$ and FF are 0.54 V, 19.7 mA·cm⁻², and 0.48, respectively. Compared with ODSSCs based on CoSe₂ and NC, the PCE increased by about 26% and 87%, respectively. This is mainly due to the best electrocatalytic activity of CoSe2-NC CE in polysulfide electrolyte. In addition, to evaluate the stability of the counter electrode in polysulfide electrolytes, a multi-cycle successive CV scanning test was carried out on a CoSe2-NC CE at a scan rate of $100 \text{ mV} \cdot \text{s}^{-1}$. After 50 cycles of successive scanning, the peak current density and curve shape remains essentially unchanged for CoSe₂-NC CE, as shown in Fig. 8b, which shows that CoSe₂-NC has excellent electrochemical stability in S_n^{2-}/S^{2-} electrolytes. Table IV summarizes the photovoltaic parameters of QDSSCs based on the same CdS/CdSe/ZnS QDs and a polysulfide electrolyte as this work in recent years. The PCE of QDSSC fabricated with CoSe2/NC CE achieves a higher value in this work.



Figure 8. (a) *J*–*V* curves of QDSSCs based on various CEs; (b) Fifty successive CV cycles for CoSe₂-NC in polysulfide electrolyte. The insets show the CV plots only for the 1st and 50th cycle.

Table III.	Photovoltaic	parameters of	CdS/CdSe (ODSCs based on	CoSe ₂ -NC	. CoSe2	. and NC CEs.
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Samples	$J_{ m sc}~(m mA \cdot m cm^{-2})$	$V_{\rm oc}$ (V)	FF	PCE (%)
CoSe ₂ -NC	19.65 ± 0.05	0.54 ± 0.02	0.48 ± 0.05	5.06 ± 0.06
CoSe ₂	18.10 ± 0.07	0.51 ± 0.02	0.43 ± 0.04	4.02 ± 0.08
NC	15.55 ± 0.05	0.45 ± 0.03	0.38 ± 0.05	2.70 ± 0.08

Table IV. QDSSCs performance comparison with recent reports of carbonaceous composite CEs.

CEs	$J_{\rm sc} ({\rm mA\cdot cm^{-2}})$	V _{oc} (V)	FF	PCE (%)	Active Area (cm ²)	References
CoSe ₂ /NC	19.65	0.54	0.48	5.06	0.25	present
						work
MnCo ₂ S ₄ /CNTs	18.45	0.58	0.45	4.85	0.16	37
CoS/NC-30	14.68	0.55	0.55	4.46	0.25	51
Cu ₂ S/CP	18.67	0.50	0.54	5.06	0.25	7
RGO/Cu ₂ S	17.11	0.58	0.48	4.76	0.16	52
FeS/C	20.33	0.44	0.51	4.58	—	53

Conclusion

The coral-like carbon framework formed by ZIF pyrolysis provides support for CoSe₂ nanoparticle loading, and the synapses and pores on the catalyst surface increase the contact with the electrolyte to facilitate the electrocatalytic reaction. In addition, CoSe₂ with excellent reducing activity towards S_n^{2-} and highly conductive N-doped porous carbon synergistically promote the performance of the hybrids. The CdS/CdSe QDSSCs with the CoSe₂-NC CE obtained a PCE up to 5.06%, which is 1.26 and 1.87 times that of CoSe₂ and NC CEs. In conclusion, the designed coral-like CoSe₂-NC hybrid is a promising material for the reduction of S_n^{2-} .

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